## **REMARKS**

Applicants have amended their claims in order to further clarify the definition of various aspects of the present invention. Specifically, claim 23 has been amended to recite that the polishing medium does not include abrasive grains; and claim 24 has been amended to delete recitation that the abrasive grains are colloidal silica or colloidal alumina, and to recite that the "polishing medium" (not the abrasive grains) has a pH of 3 or less. Claim 33 has been amended to recite that the oxidizing agent is selected from the group consisting of hydrogen peroxide, nitric acid, potassium periodate, hypochlorous acid and ozone water; and claim 34 has been amended to correct the spelling of the word "least". Claim 38 has been amended to recite a polishing-rate ratio ("Ta/SiO<sub>2</sub>") between tantalum and silicon dioxide.

Moreover, Applicants are adding new claims 41-58 to the application. Claim 41, dependent on claim 24, recites that the abrasive grains are made of colloidal silica or colloidal alumina; in this regard, note the subject matter deleted from previously considered claim 24. Claims 42-48 respectively recite subject matter expressly set forth in claims 27-33, but are dependent (ultimately) on claim 23. Claims 49 and 50, dependent respectively on claims 23 and 24, further define the pH of the medium; and claims 51-53 recite subject matter set forth in claims 38-40, respectively, but are dependent ultimately on claim 24. Claims 54 and 56, dependent respectively on claims 23 and 24, define the pH of the oxidizing agent; and claims 55 and 57, dependent respectively on claims 23 and 24, further define the pH of the oxidizing

agent. Claim 58 defines a method of polishing a member, by the use of the polishing medium for chemical-mechanical polishing according to claim 37.

Applicants respectfully traverse the rejection of claims 23 and 33 under the second paragraph of 35 USC §112, as being indefinite, set forth in Item 8 on pages 5 and 6 of the Office Action mailed January 8, 2004, especially insofar as this indefiniteness rejection is applicable to the claims as presently amended. Thus, claim 23 has been amended to recite that the polishing medium does not include abrasive grains (not gains), thereby avoiding the basis for rejecting claim 23 as indefinite. In addition, claim 33 has been amended to recite that the oxidizing "agent" is selected from the group consisting of specified agents, thereby obviating the basis for rejecting claim 33 as indefinite.

Applicants respectfully submit that all of the claims presented for consideration by the Examiner patentably distinguish over the teachings of the references applied by the Examiner in rejecting claims in the Office Action mailed January 8, 2004, that is, the teachings of the U.S. Patents to Lee, et al., No. 6,171,852, to Kaufman, et al., No. 5,954,997, and to Hardy, et al., No. 6,238,592, even in light of "admitted prior art" alleged by the Examiner, under the provisions of 35 USC §102 and 35 USC §103.

It is respectfully submitted that these references as applied by the Examiner would have neither taught nor would have suggested such a polishing medium, or such method of using this polishing medium, as in the present claims, having the recited components including the oxidizing agent for a conductor, the protective film-forming agent for protecting a metal surface and the acid, and wherein the polishing medium

has a pH of 3 or less and the oxidizing agent is in a concentration of from 0.01% by weight to 3% by weight. See claim 23; note also claim 24.

In addition, it is respectfully submitted that these applied references would have neither taught nor would have suggested such a polishing medium as in the present claims, having features as discussed in the immediately preceding paragraph, and furthermore, wherein the polishing medium does not include abrasive grains. See claim 23.

Furthermore, it is respectfully submitted that these references would have neither taught nor would have suggested such polishing medium as in the present claims, having features as discussed above in connection with claim 24, and wherein abrasive grains of the polishing medium have an average particle diameter of 50 nm or less and a standard deviation of particle size distribution in a value of more than 5 nm. See claim 25.

Moreover, it is respectfully submitted that the teachings of the applied references would have neither disclosed nor would have suggested such a polishing medium, or such method of polishing a substrate using such medium, as in the present claims, wherein the medium has a polishing-rate ratio between tantalum and copper or a copper alloy of more than 1, a polishing-rate ratio between tantalum nitride and copper or a copper alloy of more than 1, a polishing-rate ratio between tantalum and silicon dioxide of more than 10, and a polishing-rate ratio between tantalum nitride and silicon dioxide film of more than 10. See claim 37; note also claims 38-40, 51-53 and 58.

In addition, it is respectfully submitted that the teachings of the applied prior art would have neither disclosed nor would have suggested the presently claimed invention, including features as discussed previously in connection with claims 23 and 24, and furthermore wherein the polishing medium additionally includes a water-soluble polymer (note claims 27 and 42), particularly the water-soluble polymer as in claims 28 and 43, and wherein the oxidizing agent is included in a concentration of from 0.01% by weight to 1.5% by weight (see claims 29 and 44); and/or wherein the acid of the polishing medium is an organic acid (see claims 30 and 45), particularly wherein the acid is at least one selected from the group thereof listed in claims 31 and 46; and/or wherein the protective-film-forming agent is at least one selected from the group set forth in claims 32 and 47; and/or wherein the oxidizing agent is selected from the group as set forth in claims 33 and 48; and/or materials of the conductor (for which the first-named agent in claims 23 and 24 is an oxidizing agent), as set forth in claims 34-36; and/or the further definition of the pH of the medium as in claims 49 and 50, or pH of the oxidizing agent as in claims 54-57.

The present invention is directed to a polishing medium for chemical-mechanical polishing, especially suitable for polishing when forming wirings of semiconductor devices, and a method of polishing using this medium.

In buried-metal formation as in the formation of damascene wirings of copper or copper alloy or the formation of plug wirings of tungsten, a phenomenon called "thinning" in which the thickness of wiring becomes small together with an interlaminar insulating film may occur when an interlaminar insulating film of, e.g., silicon dioxide, is

polished at a rate close to the rate of polishing the metal film. As a result, there may be caused an increase in wiring resistance or a non-uniformity in resistance ascribable to pattern density. Hence, it is desired that the polishing medium for chemical-mechanical polishing have a property that the polishing rate of a silicon dioxide film is sufficiently smaller than that of the metal film to be polished. Note the last paragraph on page 5 of Applicants' specification.

It is also desired that in performing the metal polishing, "dishing" of the surface of the metal wiring, wherein the surface becomes hollow at the middle thereof like a dish, resulting in a bad effect on flattening, be avoided.

In chemical-mechanical polishing of, e.g., a layer of copper or copper alloy of wiring, together with polishing of, e.g., a layer of tantalum, tantalum alloy, tantalum nitride or other tantalum compound as a barrier layer, a two-step polishing method has been proposed, having a first step of polishing the copper or copper alloy and a second step of polishing the barrier layer conductor. In this two-step method, and in particular in the second step of polishing the tantalum-containing material, used for the barrier layer, it is important to polish the barrier layer without thinning the silicon dioxide film, and also while avoiding dishing of copper-containing material of the wiring. Note, in particular, the paragraph bridging pages 6 and 7 of Applicants' specification.

Against this background, and as a result of extensive studies performed by the present inventors, the inventors have discovered that the polishing of the tantalum-containing materials proceeds with ease when the <u>polishing medium</u> has <u>both</u> a low pH <u>and</u> the oxidizing agent is included in the medium in a low concentration. Thus,

according to the present invention, Applicants provide a polishing medium having specified components, including an oxidizing agent and a protective-film-forming agent, wherein the polishing medium has a pH of 3 or less and the oxidizing agent is included in a concentration of from 0.01-3% by weight, achieving objectives of the present invention of a relatively high polishing rate of the material of the barrier layer, while avoiding dishing and thinning respectively of the, e.g., copper wiring and of the oxide insulatator, and which additionally can avoid scratches from occurring in the wirings. Thus, as described on pages 8 and 9 of Applicants' original disclosure, the present inventors have discovered that the polishing of the tantalum, tantalum alloy, tantalum nitride and other tantalum compounds which are used as the barrier layer proceeds with ease in a low pH range and where the oxidizing agent is included in the medium at a low concentration. Moreover, at such pH and low concentration of the oxidizing agent, etching rate of copper or copper alloy does not increase, avoiding dishing problems.

More specifically, as described in the sole full paragraph on page 16 of Applicants' specification, in general when the polishing medium has a pH of less than 3, etching rate of the copper or copper alloy film is so high as to make it difficult for the protective-film-forming agent to control the etching. However, in the present invention, the concentration of the oxidizing agent is so sufficiently low that the protection-film-forming agent can control the etching.

Furthermore, by utilizing abrasive grains having an average particle diameter as in various of the present claims, the polishing rate of silicon dioxide is decreased,

avoiding any "thinning" problems. See the paragraph bridging pages 21 and 22 of Applicants' specification.

Lee, et al. discloses a chemical-mechanical abrasive composition, useful in polishing the surface of a semiconductor wafer, which includes 70-95% by weight of an aqueous medium; 1-25% by weight of an abrasive; and 0.1-20% by weight of an abrasion accelerator, wherein the abrasion accelerator comprises a monocarboxy group-or an amido group-containing compound and optionally a nitrate salt. The chemical-mechanical abrasive composition can further include an anionic surfactant, such as polycarboxylic acid or polyacrylic acid copolymer, or the salts thereof, to reduce viscosity of the abrasive composition. See column 2, lines 37-39. This patent further discloses that the composition can further include 1-15% by weight, and preferably 4-8% by weight, of an oxidant. See column 2, lines 63-65. Note also column 3, lines 3-7, for various oxidants. This patent further discloses that when used in a copper production process, the abrasive composition may include benzotriazole and/or its derivatives to inhibit rapid copper erosion. Note column 4, lines 13-20. In Example 1 of Lee, et al., the slurry is disclosed as having a pH of about 3.8. In Example 9 in column 8, a slurry also having a pH of 3.8 is described. In Example 3 bridging columns 5 and 6 of this patent, it is described that the slurry was adjusted with HNO<sub>3</sub> and NH<sub>4</sub>OH to have a pH of about 2.2. This abrasive slurry of Example 3 included silica abrasive particles, in a solid content of the slurry being 6 wt.%; and 3 wt.% ammonium nitrate and 3 wt.% urea.

It is emphasized that in Lee, et al., use of a composition including 1-15%, preferably 4-8%, by weight of an oxidant, is disclosed; and, moreover, various of the examples have a pH greater than 3. It is noted that the express disclosure of a pH less than 3 is in Example 3. Particularly in view of preferred ranges for the oxidant as in Lee, et al., and disclosure of pH greater than 3.0, it is respectfully submitted that this reference does not disclose, nor would have suggested, the presently claimed subject matter, including both the pH of range and the concentration of oxidizing agent, in the polishing medium including, in addition to the oxidizing agent, the protective-film-forming agent, acid and water, and advantages achieved thereby as discussed in the foregoing.

As to these present advantages, attention is respectfully directed to Tables 2 and 3 on pages 32 and 33 of Applicants' specification, reporting on the results, including dishing and thinning levels, of examples described from page 26 of Applicants' specification. It is respectfully submitted that the results shown in these tables constitute evidence that must be considered in determining patentability of the presently claimed subject matter. See In re DeBlauwe, 222 USPQ 191 (CAFC 1984). Properly considering this evidence, it is respectfully submitted that this evidence supports patentability of the presently claimed subject matter, having both the relatively low pH and relative low concentration of oxidizing agent, as well as other features of the present invention, as in various of the present claims.

In particular, attention is respectfully directed to the explanation from page 33, line 3 to page 35, line 3, in Applicants' specification, describing the results achieved in

the Examples. This explanation supports the conclusion of unexpectedly better results achieved according to the present invention, having features as recited in the present claims.

The contention by the Examiner in Item 2 on page 2 of the Office Action mailed January 8, 2004, that Lee, et al. describes a polishing composition within the scope of the present claims, is respectfully traversed. Clearly the oxidizing agent of Lee, et al., while overlapping in some respects the concentration of oxidizing agent according to the present invention, would include much greater amounts of the oxidizing agent, and thus clearly does <u>not</u> anticipate the presently claimed subject matter. Furthermore, it is respectfully submitted that the abrasives of Lee, et al. would not satisfy the polishing rates defined by various of the present claims (note, e.g., 37).

Furthermore, it is respectfully submitted that the compositions of Lee, et al. as set forth in the Examples thereof, do <u>not</u> disclose, nor would have suggested, a medium satisfying <u>both</u> the concentration of the oxidizing agent <u>and</u> pH of the medium, and/or pH of the oxidizing agent, <u>and which also contains a protective-film-forming agent</u>, as in the present claims.

In various examples (note, for example, Example 1) of Lee, et al., the pH is 3.8, 9% alumina abrasive grains were incorporated, and <u>no</u> protective-film-forming agent is used. In addition, the concentration of the oxidizing agent is 5-10%. It is expected that the polishing rate of the copper would disadvantageously be fast through use of these media, disadvantageously providing, e.g., a dishing effect.

In Examples 3 and 5-8 of Lee, et al., amount of abrasive silicon incorporated is, e.g., 6-10%. In view thereof, the polishing rate of the silicon oxide would be fast.

Moreover, without a protective-film-forming agent, the polishing rate of the copper would be fast, causing, e.g., dishing; thus, using the compositions from the examples of Lee, et al., Lee, et al. would have neither disclosed nor would have suggested the present invention including pH and concentrations, with the medium also containing a protective-film-forming agent, achieving advantages of the present invention as discussed previously.

at 12 19

Kaufman, et al. discloses a chemical-mechanical polishing slurry which includes a complexing agent, at least one oxidizer, at least one abrasive and a film forming agent, the slurry being disclosed as useful for polishing metal layers and thin films associated with semiconductor manufacturing. This patent discloses that the slurry described in the patent has a low insulator polishing selectivity while exhibiting high polishing selectivity towards copper and copper alloy containing metal layers, embodiments of the slurry being described in column 4, lines 9-21. Note also column 5, lines 15-18, 32-39, 44, 45, 50-55 and 60-63; column 6, lines 17-25; and column 8, lines 36-42 of this patent. This patent also discloses that it is desired to maintain the pH of the slurry within a range of from about 2.0 to about 4.0, preferably between from about 4.0 to about 9.0, in order to facilitate control of the polishing process. See column 8, lines 23-26. Note also Example 1 and the description in connection therewith at column 9, lines 45-49, disclosing that the slurry has a pH of 5.1; and Example 2,

particularly at column 10, lines 27 and 28, disclosing slurries having a pH ranging from 7.2-7.8.

e: 40 %

Noting the relatively high pH at the upper limit of the pH range for the slurry in Kaufman, et al., it is respectfully submitted that while there may be some overlap of the range for pH in Kaufman, et al. and the range according to the present invention, Kaufman, et al. would have neither disclosed nor would have suggested a slurry as in the present claims, including <a href="both">both</a> the relatively low pH range <a href="and-relatively-low-concentration">and-relatively-low-concentration</a> of oxidizing agent, in the present medium, and advantages achieved thereby, as discussed in the foregoing.

Moreover, note that in the examples of Kaufman, et al., concentration of the oxidizing agent is from 2-30%, and thus relatively high values are employed. Such relatively high concentration of oxidizing agent, with pH values as in Kaufman, et al., would have neither disclosed nor would have suggested the presently claimed subject matter, including advantages achieved thereby.

It is respectfully submitted that the additional teachings of Hardy, et al. would <u>not</u> have rectified the deficiencies of Lee, et al. or Kaufman, et al., such that the presently claimed subject matter would have been obvious to one of ordinary skill in the art.

Hardy, et al. discloses a working liquid useful in modifying a surface of a wafer suited for fabrication of a semiconductor device, the liquid being a solution of initial components comprising an oxidizing agent; an ionic buffer; a passivating agent; a chelating agent selected from iminodiacetic acid and salts thereof; and water. Note column 3, lines 29-39. This patent discloses that this working liquid can be used with a

three-dimensional abrasive article which contacts the material to be polished. Note column 4, lines 19-33. Note also column 3, lines 40-45, for the passivating agent used according to Hardy, et al. See also column 7, lines 19-30, and the paragraph bridging columns 7 and 8, of this patent. Hardy, et al. discloses that inorganic particulates may also be included in the working liquid, with the average particle size of these inorganic particulates being less than 1,000 Angstroms. See the paragraph bridging columns 9 and 10 of this patent.

Even assuming, <u>arguendo</u>, that the teachings of Hardy, et al. were properly combinable with the teachings of either of Lee, et al. or Kaufman, et al., it is respectfully submitted that the combined teachings of these references would have neither disclosed nor would have suggested use of <u>both</u> the medium having <u>both</u> the relatively low pH <u>and</u> relatively low concentration of oxidizing agent, in the medium of the present invention, and advantages thereof; or the other aspects of the present invention as discussed previously, and advantages thereof.

Furthermore, it is respectfully submitted that none of the references refer to etching rate ratios; and it is respectfully submitted that none of the applied prior art would have disclosed, or would have suggested, a medium and/or method as in the present claims, with etching rate ratios as in various of the present claims.

In particular, even in view of any possible "admitted prior art", it is respectfully submitted that Lee, et al. and such "admitted prior art" would have neither disclosed nor would have suggested a medium, or method of polishing therewith, having the components of the medium with a pH and relatively low concentration of oxidizing agent

as in the present claims, and with etching rate ratios as in various of the present claims, and advantages thereof.

In view of the foregoing comments and amendments, reconsideration and allowance of all claims remaining in the application, are respectfully requested.

To the extent necessary, Applicants petition for an extension of time under 37 CFR 1.136. Please charge any shortage in fees due in connection with the filing of this paper, including extension of time fees, to the Antonelli, Terry, Stout & Kraus, LLP Deposit Account No. 01-2135 (Docket No. 566.41191X00), and please credit any excess fees to such Deposit Account.

Respectfully submitted,

ANTONELLI, TERRY, STOUT & KRAUS, LLP

William I. Solomon

Registration No. 28,565

1300 North Seventeenth Street

**Suite 1800** 

Arlington, VA 22209 Tel.: 703-312-6600

Fax.: 703-312-6666

WIS/sjg